THE THERMOCHEMICAL CONVERSION OF CELLULOSE TO OIL IN DIFFERENT SOLVENT-FEED RATIOS WITH DIFFERENT REDUCING GASES.

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ABSTRACT

The conversion of cellulose (Solkaflock) with different aqueous feed ratio with 35 bar reducing gases (H_2 and CO) were studied in a batch autoclave system at 350°c in presence of 5% Pt/Al_2O_3 catalyst. Under these conditions, the conversion showed a general increase with increasing solvent/feed ratio, but more significantly when CO was used as the reducing gas. This is perhaps due to the better contact between the feed and catalyst as well as greater amount of solvent space. Decomposition of cellulose yielded mainly oil of relatively low oxygen content and high heating value. Increasing S/F ratio were produced lower amounts of oil and char but increasing the higher yields of water-soluble fractions. This is probably due to the higher liquefaction of gaseous products. Moreover, the oil were obtained from 10:1 (S/F ratio with H_2 gas) was contained 20.0% lights in comparison with 6:1 (S/F ratio with H_2 gas) contained 56.0% lights which is due to higher methanation reactions in 10:1 S/F ratio.

INTRODUCTION:

The effect of water to wood ratio has been found to be an important parameter during liquefaction with Na_2CO_3 and CO (1). In run 1, 2, 3, and 4, the effect of solvent /feed ratio, on the liquefaction of cellulose was studied using 5% Pt/Al_2O_3 catalyst in presence of CO and H_2 as reducing gases with water into fuels.

EXPERIMENTAL PROCEDURE:

These experimental works were conducted with 1-liter rocker stainless steel autoclave reactor. cellulose, catalyst and water were charged to it. Hydrogen or Carbon monoxide was added to the desired pressure (35 bar) and the autoclave was then brought to operating temperature at 350°c. and reaction time was 2 hours. After cooling the autoclave, the product gas was collected in a gas measurement system and were analyzed by GC. The aqueous phase was separated by decantation and the remaining oil and solids were removed by adding acetone, then were refluxed for 6 hours. Then filter it with filter paper by water vacuum. The residue is char and catalyst, was dried in an oven at 110°c for overnight. The filtrate was oil and acetone. The oil was recovered from acetone by rotaevaporation. These oil were further separated into lights, waxes by using solvent- heptane and then separated into asphaltene, resins,by using toluene. The feed, char, and oils were analyzed by elemental analyser.

RESULTS AND DISCUSSIONS:

The reaction inputs, operating parameters and products distribution were shown in Table 1; and depicted graphically in Figure 1.

From the Table 3, the elemental analysis, it is seen that an increase in the H/C atomic ratio and a decrease in O/C atomic ratio as S/F changed from 6:1 to 10:1 in oils of runs 1 and 2 which indicate that increasing S/F ratio did not really promote the quality of oils.

The oil obtained from run 1 contained 56.0% light volatile whereas run 2 contained 20.0 %. Also, both Asphaltenes and resins of run 2 were greater in yields than those of run 1 which is

due to higher methanation ($CO + H_2 \longrightarrow CH_4$) reactions in run 2, that is more hydrogen consumed to form CH_4 not to hydrogenation with heavier fractions like Asphaltenes and resins.

However, in runs 3 and 4; both of which involved the use of CO as reducing gas. More lights 59.0% and smaller amounts of resins 17.2% and asphaltenes (11.5%) were produced relative to those of run 3; which probably the water-gas shift reaction was greater because of the greater volume of water present.

$$CO + H_2O \longrightarrow CO_2 + H_2$$
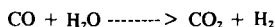
Therefore, the hydrogen is produced in situ which could have gained access to the sites and substrate molecules faster than the hydrogen present in the gaseous phase.

The calorific value of oil in run 1 is 7.840 Kcal/g (S/F ratio, 6:1) which is higher than that in run 2, 7.730 Kcal/g (S/F ratio, 10:1) when hydrogen is used as reducing gas. On the other hand, when CO is used as reducing gas, the calorific value of oil in run 4, (S/F ratio 10:1) is 8.530 Kcal/g is higher than that in run 3, (S/F ratio 6:1), 7.620 Kcal/g which is not likely as before. In both the cases, the increase in calorific value was probably due to higher yields of lighter materials in the oils and not to changes in S/F ratio.

The IR spectra and GC analysis of product gases in figure 3 and product gas distribution in table 5 is seen that run 3 and 4 were produced higher yields of CO_2 than run 1 & 2 because of predominance of the water-gas shift reaction in the CO atmosphere.

Run 2 produces higher yields of hydrocarbon gases which may probably the activity of the catalyst in hydrogen atmosphere.

In run 4, was produced low yield of hydrogen 3.14%, in comparison with run 3, 15.22%, may probably the reactivity of hydrogen produced in situ. If hydrogen was used up as postulated, then lower yields were expected.

The solvent water is a necessary component of the mixture undergoing the oil forming reaction. The source of water are as follows:

(a)   First, most substrates contain large amounts of moisture.

(b)   Second, since most organic wastes are highly oxygenated, water is formed merely by heating them to reaction temperature; so it is a reaction product.

(c)   Third, added to the reaction mixture as a solvent.

Moreover, Water acts as a solvent, vehicle and reactant. Solvation can occur between the hydroxyl groups of the substrate and water. It is an excellent medium for intermediate hydrolysis of cellulose and other high molecular-weight carbohydrates to water soluble sugars. The primary reactions in the conversion to oil likely involve formation of low molecular-weight, water soluble compounds such as glucose or pyruvic acid.

Water is a mechanical vehicle for facilitating mixing of reactants and preventing condensations to char by diluting the intermediates. Water acts as a reactant. The hydrogen added to the substrate comes from water, which consumes carbon monoxide by reacting with it to form carbon-di-oxide and hydrogen (Water gas shift reaction).

CONCLUSION:

1)   Lower S/F ratio resulted in greater yields of gaseous products, oil and chars. Higher S/F ratio resulted in greater yields of water solubles and water.

2)   O/C atomic ratio decreased with increase in S/F ratio.

3)   Changes in S/F ratio had no direct effect on the calorific values of the oils.

4)   Under CO atmosphere, when the S/F ratio was 6:1, the product of gases were contained a higher percentage of H_2 (15.22%) than S/F ratio 10:1 (3.14%).

5)   The high partial pressure of steam raises the operating pressure to levels where capital costs would be high.

6)   The heat required to bring water to the operating temperature and pressure adds considerably to the operating costs and

7)   The separation of the oil and water phases during the product recovery step is sometimes encumbered by emulsions.

8)   In case of tetralin, it can participate with the reaction at low temperature as well as low partial pressure raised; although water is more cheaper than tetralin.

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APPENDEX:

Table: 1   Reaction Inputs , Parameters and Product distribution

Run	1	2	3	4
Feed type (Solkaflock)	6:1	10:1	6:1	10:1
Feed (g)	40.0	40.8	40.0	40.8
Catalyst	5% PVAl$_2$O$_3$	5%PVAl$_2$O$_3$	5%PVAl$_2$O$_3$	5%PVAl$_2$O$_3$
Catalyst (g)	1.0	1.0	1.0	1.0
Suspension medium-water(g)	240.0	408.0	240.0	408.0
Reducing gas	H$_2$	H$_2$	CO	CO
Reducing gas (g)	2.09	1.6	29.34	22.40
TOTAL INPUT (g)	283.13	451.40	310.34	471.9
Temperature (°C)	350	350	350	350
Initial Pressure (atm.)	35	35	35	35
Heating up time (hr.)	2.2	2.0	2.0	2.0
Reaction time (hr.)	2.0	2.0	2.0	2.0
Max. Reaction Press. (atm.)	200.0	250.0	210.0	255.0
Final Reaction Press. (atm.)	22.0	18.0	35.0	40.0
TOTAL OUTPUT (g)	275.2	447.6	295.7	470.0
% Recovery from Autoclave	97.2	99.20	95.28	99.60
Product Distribution				
Gas recovered (g)	9.5	8.0	28.7	27.20
Water-soluble fraction (g)	3.3	12.0	4.5	14.0
Oil (g)	12.4	9.5	8.5	8.0
Char + Catalyst (g)	3.0	2.3	7.5	2.0
Water-recovered (g)	247.0	416.0	246.5	418.6
Water-Produced (g)	7.0	6.0	6.5	10.6
% Gas Produced (g)	18.42	15.68	16.50	12.5
% Water-soluble fraction	8.25	29.41	11.25	34.3
% Oil	31.0	23.28	21.25	19.60
% Char	5.0	3.18	18.25	2.40
% Water-Produced	17.5	19.60	16.25	26.47
% TOTAL RECEIVED	80.17	91.15	81.50	95.27
% CONVERSION	92.37	95.51	75.25	96.23

Table 2.   Product of gas recovery

Run	S/F* ratio	Conversion %	Initial gas (g)	Gaseous Product				
				Vol at S.T.P.	Mol. wt.	wt. (g)	Net wt.	% Prod'd
1	6:1	94.37	2.13	7.3	29.4	9.5	7.37	18.42
2	10:1	95.51	1.6	6.9	26.0	8.0	6.4	15.68
3	6:1	75.25	22.1	15.0	43.0	28.7	6.6	18.50
4	10:1	96.23	22.1	14.5	42.0	27.2	5.1	12.5

* Solvent/Feed ratio

Table no.   3. Elemental Analysis

Run	S/F ratio	Initial Press. (atm.)	Temp. (°C)	Feed Type	% Conversion	Feed stock					Char analysis					Oil analysis					H/C	O/C	Calorific value (Kcal/g)
						% C	% H	% N	% O*	% Ash	% C	% H	% N	% O*	% Ash	% C	% H	% N	% O*	% Ash			
1	6:1	35 (H_2)	350	Cellulose	92.37	41.5	6.1	ND	52.4	ND	63.3	5.7	0.2	30.0	0.8	72.1	6.9		19.7	NO	1.14	0.20	7.840
2	10:1	35 (H_2)	350	Cellulose	95.51	41.5	6.1	ND	52.4	ND	58.4	4.8	0.8	32.0	4.0	74.0	7.8		18.0	0.2	1.28	0.18	7.730
3	6:1	35 CO	350	Cellulose	75.25	41.5	6.1	ND	52.4	ND	63.2	4.0	0.3	25.0	7.5	73.2	7.2		18.5	0.5	1.17	0.19	7.620
4	10:1	35 CO	350	Cellulose	96.23	41.5	6.1	ND	52.4	ND	63.7	6.0		30.3		71.2	7.5		19.0	2.3	1.25	0.20	8.530

S/F ratio = Solvent/Feed ratio

* Estimated by difference

Table no.   4. Product oil composition

Run	Initial Press (atm.)	Temp. (°C)	Feed Type	Product oil composition				Elemental analysis											
								Heptane Soluble (boil)				Toluene soluble				Toluene insoluble			
				Heptane Soluble (%) Light volatiles	Heptane Soluble (boil) (%) (Waxes)	Toluene Soluble (%) (Asphaltenes)	Toluene Insoluble (%) (Resins)	% C	% H	% O	% Ash	% C	% H	% O	% Ash	% C	% H	% O	% Ash
1	35 H_2	350	Cellulose	56.0	14.5	17.2	12.3	82.2	7.5	10.3	ND	80.2	6.5	2.8	10.5	76.8	6.5	1.5	15.2
2	35 H_2	350	Cellulose	20.0	3.0	45.0	32.0	75.0	5.0	20.0	—	70.0	5.5	11.0	13.5	68.5	6.2	2.0	23.3
3	35 CO	350	Cellulose	46.4	7.5	28.3	17.8	79.7	7.8	12.0	0.5	70.7	7.9	19.0	2.4	78.0	5.8	16.0	0.2
4	35 CO	350	Cellulose	59.0	12.3	11.5	17.2	72.5	4.8	20.7	2.0	69.2	5.0	22.3	3.5	66.5	5.5	2.8	25.2

Table   5. Product of gas distribution

Run	1	2	3	4
Temperature (°C)	350	350	350	350
Pressure (atm)	35	35	35 (CO)	35 (CO)
S/F ratio	6:1	10:1	6:1	10:1
Gas	H_2	H_2	CO	CO
% CO_2	28.83	17.70	58.16	71.12
%CO	48.14	25.22	24.51	22.86
%CH_4	0.082	1.58	0.91	2.14
% C_2H_6	0.039	0.53	0.25	0.60
%C_2H_4	0.044	0.05	0.28	0.0*
%C_3H_8	0.049	0.57	0.31	0.03
%C_3H_6	0.0124	0.01	0.08	0.01
% Butane	-	0.03	-	-
% Isobutylene	-	-	-	-
% 1-Butene	-	-	-	-
% Cis-2-butene	0.0233	0.07	0.12	0.03
% Trans-2-butene	0.0398	0.05	0.08	0.04
% Butadiene	0.0050	0.03	0.08	
% Total	77.27	45.84	84.78	96.86
% H_2+uP, *	22.72	54.16	15.22	3.14

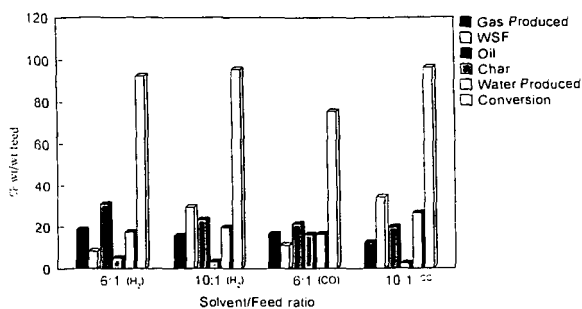* % H_2 + Unidentified Peaks were estimated by difference.

Fig. 1.The effect of S/F ratio on H₂ and CO reducing atmosphere
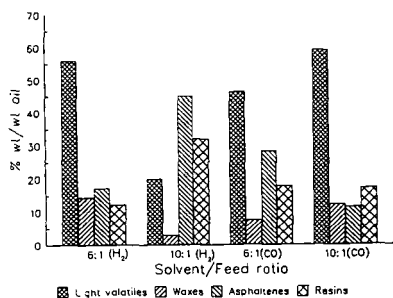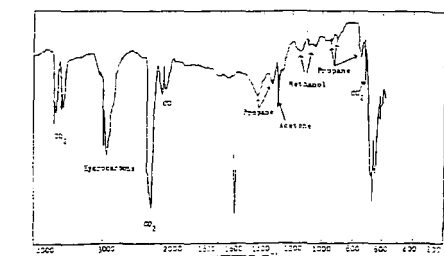

Fig. 2.The Effect of reducing gas on S/F on the Product oil Composition

Injected Sample = 18.0cmHg

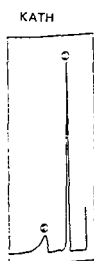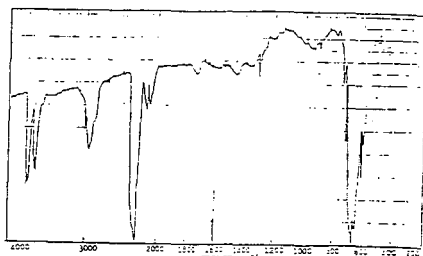| Peak No.	Gas	RT(min)
1	CO	0.98
2	CO₂	2.45
3	CH₄	1.00
4	C₂H₆	1.55
5	C₂H₄	2.15
6	C₃H₈	2.75
7	C₃H₆	6.60
8	n-Butane	7.40
9	Cis-7-butene	12.45
10	Trans-2-butene	12.30
11	Butadiene	11.75
12	Unknown	
13	Unknown	
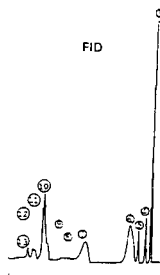
Fig. 3 : The IR spectrum and GLC chromatograms of the gaseous product from Run 1

Injected Sample = 17.5cmHg

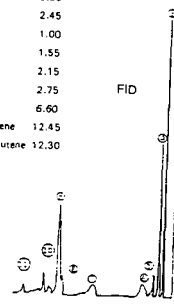| Peak No.	Gas	RT(min)
1	CO	0.98
2	CO₂	2.45
3	CH₄	1.00
4	C₂H₆	1.55
5	C₂H₄	2.15
6	C₃H₈	2.75
7	C₃H₆	6.60
8	Cis-2-butene	12.45
9	Trans-2-butene	12.30
10	Unknown	
11	Unknown	

Fig. 4 : The IR spectrum and GLC chromatograms of the gaseous product from Run 4